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Self-assembling of cholesterol-appended benzothiadiazole–triphenylamine two-photon absorption dye

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ABSTRACT

Cholesterol-appended benzothiadiazole–triphenylamine two-photon absorption dye was prepared and its self-assembling nature was investigated. The dye gave viscous fluid organogels in aliphatic hydrocarbon solutions such as cyclohexane, in which one-dimensional supramolecular aggregates are formed through the van der Waals interactions among the cholesterol moieties and the intermolecular hydrogen-bonding interactions among the carbamate spacer moieties. The supramolecular self-assembling was confirmed by the line-broadening effect in the ^{1}H NMR spectra, and by the bathochromic shifts of the absorption and emission bands. The bathochromic shift of the absorption band suggested that the benzothiadiazole–triphenylamine moieties take a *J*-like aggregation mode. Under the self-assembled conditions, the dye showed a negative exciton splitting pattern in the CD spectrum, suggesting the one-dimensional stacking with a left-handed twisting mode. The two-photon absorption nature in the parent benzothiadiazole–triphenylamine chromophore is maintained in the self-assembled system.

1. Introduction

Supramolecular self-assembly composed of organic π-conjugated molecules has been of much interest in view of their potential application to material sciences [1–8]. Benzothiadiazole dyes and their derivatives are attractive candidates of the organic π-conjugated molecules, because of their strongly electron-accepting nature [9,10]. In addition, the dyes provide another character of strong light-emitting ability both in solution and solid state [11,12]. On the other hands, two-photon absorption dyes can be created by simple strategy on the basis of a connection between donor and acceptor moieties, by which the intramolecular charge-transfer character is enhanced to generate two-photon absorption nature [13,14]. Recently, we have created benzothiadiazole-based two-photon absorption dyes with light-emitting ability on the basis of a combination of the electron-withdrawing benzothiadiazole core and electron-donating triphenylamine moieties [15]. Then, the two-photon absorption dyes were developed to functional systems such as two-photon-excited red fluorescence emitting system [16], two-photon-induced single oxygen sensitizing system [17], and two-photon-triggered emitting OFF–ON system [18]. In the application to the functional two-photon absorption materials, an ordered arrangement of the two-photon absorption dyes is important to enhance the functionalities as well as to generate a new functionality. In this paper, we report the first finding of an arrangement of the benzothiadiazole–triphenylamine dye via supramolecular self-assembling. The strategy is based on the introduction of the four self-assembling cholesterol moieties [19,20], which are appended to a benzothiadiazole core through hydrogen-bonding carbamate moieties.

2. Experimental

2.1. General

All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer and measured as KBr pellets. ^{1}H NMR spectra were determined in $CDCl_3$, CD_2Cl_2, and cyclohexane-d_{12} with a JEOL JNM-AL 400 spectrometer. Residual solvent protons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (*J*) are reported in hertz (Hz).

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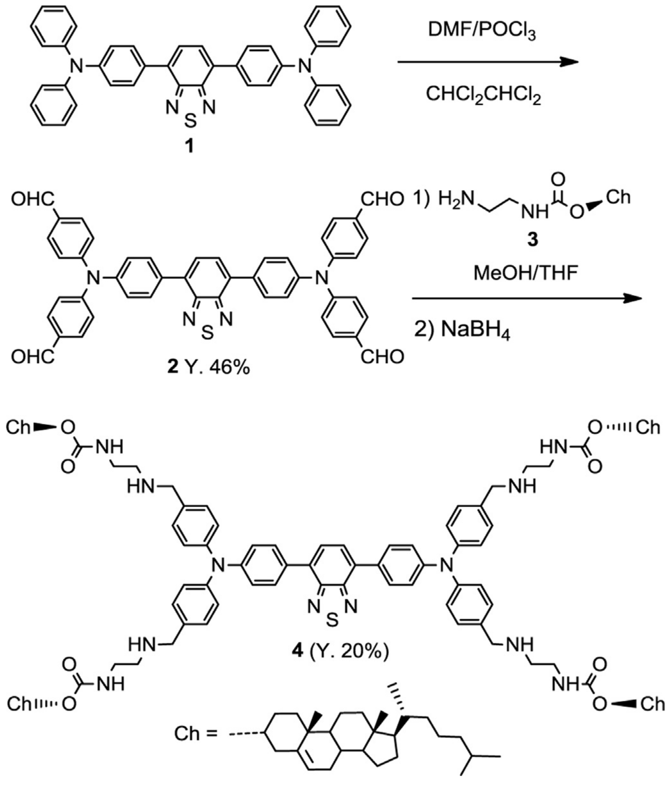

Scheme 1. Preparation of **4**.

Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a BRUKER Auto FLEX spectrometer using delayed extraction mode and with an acceleration voltage of 20 keV. Samples were prepared from a solution of dichloromethane using dithranol as the matrix.

Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F_{254}). Column chromatography was carried out on silica gel (WAKO C300). DMF was distilled from calcium hydride under reduced pressure, and stored under an argon atmosphere. 1,1,2,2-Tetrachloroethane was distilled from calcium hydride under an argon atmosphere just before use. THF was distilled from sodium and benzophenone under an argon atmosphere just before use. Methanol was dried over 4A molecular sieves. Preparation of **1** [16] and **3** [21] was reported previously.

Table 1
Organic solvents tested for gelation by **4**.[a]

Solvent	20 °C (5 °C)
Hexane	I
Cyclohexane	S (G)
Methylcyclohexane	S (*p*G)
Benzene	S
Toluene	S
Methanol	I
Ethanol	I
Dichloromethane	S
Chloroform	S
1,2-Dichloroethane	S (R)
1,1,2,2-Tetrachloroethane	S
Acetone	I
Ethyl acetate	R
Acetonitrile	I
DMSO	*p*G
1,4-Dioxane	S (R)
1-Butanol	R
2-Propanol	R
NMP	*tp*G

[a] [**4**] = 10.0 mM; G = gel, *p*G = partial gel, *t*G = turbid gel, *tp*G = turbid partial gel, R = recrystallization, S = solution, I = insoluble.

2.2. *Spectroscopic measurement*

UV–vis spectra were measured on a JASCO V-570 spectrophotometer in 0.01 cm width quarts cell (1.0 mM), 0.1 cm cell (0.1 mM), and 1.0 cm cell (0.01 mM). Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer. Film samples for the measurements of UV–vis and fluorescence spectroscopy were prepared by drop casting and the subsequent spin-coating (2000 rpm, 30 s) from cyclohexane solutions (100 μL) on quartz cell (12.5 × 12.5 × 45 mm). CD spectra were measured on a JASCO J-715 spectropolarimeter in 0.1 cm width quarts cell (1.0 mM). Atomic force microscopy (AFM) images were obtained on an SII SPA400 DFM (tapping mode). SI-DF20 type tips were used. Samples were prepared by drop casting from 0.001 mM cyclohexane solution on freshly cleaved mica. Two-photon absorption cross-sections were measured by using an open aperture Z-scan method with femtosecond pulses from an optical parametric amplifier (Quantronix TOPAS) excited by an 1 kHz repetition Ti:sapphire regenerative amplifier system (Quantronix Integra). The pulse width is 120 fs and the spatial profiles were characterized by knife-edge method and can be a Gaussian profile [16]. The two-photon absorption cross-sections were estimated on the basis of AF-50 (45 GM) used as a two-photon absorption benchmark [22].

2.3. *4,7-Bis{4-[N,N-bis(4-formylphenyl)amino]phenyl}-2,1,3-benzothiadiazole (**2**)*

To a solution of **1** (873 mg, 1.40 mmol) and dry DMF (4.34 mL, 56.0 mmol) in dry 1,1,2,2-tetrachloroethane (6 mL) was added dropwise $POCl_3$ (2.61 mL, 28.0 mmol) at 0 °C, and the mixture was heated at 90 °C for 4 days. During the heating, a mixture of dry DMF (1.30 mL, 16.8 mmol) and $POCl_3$ (0.80 mL, 8.4 mmol) in dry tetrachloroethane (0.9 mL) was added three times after 1, 2, and 3 days. The reaction mixture was poured into ice water, neutralized with aqueous 1 N NaOH solution, and extracted with chloroform. The combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue including tetrachloroethane was passed through a short pad of silica eluting with chloroform and the filtrate was evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography eluting with chloroform to give **2** in 46% yield (473 mg, 0.64 mmol): Pale orange powder; mp 226–228 °C; IR (KBr, cm^{-1}) 3032, 1693 ($\nu_{C=O}$), 1588, 1505, 1480, 1321, 1283, 1215, 1163, 825; ^1H NMR ($CDCl_3$) δ 7.23–7.38 (m, 12 H, ArH), 7.83 (d, $J = 8.6$ Hz, 8 H, ArH), 7.85 (s, 2 H, ArH), 8.04 (d, $J = 8.6$ Hz, 4 H, ArH), 9.93 (s, 4 H, CHO); FAB-MS (NBA, positive) m/z 734 (M^+). Anal. Calcd for $C_{46}H_{30}N_4O_4S$: C, 75.19; H, 4.12; N, 7.62; Found: C, 75.00; H, 4.03; N, 7.65.

2.4. *4,7-Bis{4-[2-(3β-cholest-5-en-3-ylcarbamate-N-yl)ethylamino methyl]phenyl}-2,1,3-benzothiadiazole (**4**)*

To a suspension of **2** (147 mg, 0.20 mmol) in dry THF (4 mL) and dry methanol (4 mL) was added **3** (416 mg, 0.88 mmol) at room temperature under an argon atmosphere, then the mixture was heated at 50 °C for 4 h. The imination reaction was monitored by the measurement of ^1H NMR ($CDCl_3$), which indicated the disappearance of